

Synthesis, characterization and electrochemical studies on novel Li_2MZrO_4 (M = Fe, Mn) cathode material for lithium-ion battery

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ABSTRACT

We report a novel cathode of the molecular formula, Li_2MZrO_4 (M = Fe, Mn), based on an inexpensive, earth-abundant, and eco-friendly materials, which have theoretical capacities within 119 – 238 mAh.g^{-1} depending on the number of lithium ions extracted from material, suitable for high power rechargeable lithium-ion battery. X-ray diffraction (XRD) revealed tetragonal crystal structure of the synthesized material. SEM images illustrate the formation of porous material with large surface area. The cyclic voltammograms of Li_2MZrO_4 (M=Fe, Mn) showed only one pair of redox peak corresponding to the anodic and cathodic reactions within a potential window of 2.2 – 4.5 volts vs. Li/Li^+ . The first discharge capacities were 89 mAhg^{-1} for $\text{Li}_2\text{FeZrO}_4$, whereas in case of $\text{Li}_2\text{MnZrO}_4$ it was 94 mAhg^{-1} at 0.1 C rates, which are equivalent to removal of one lithium ion from the compounds. Copyright © 2016 VBRI Press.

Keywords: SEM; Li_2MZrO_4 (M = Fe, Mn) new cathode; powder XRD; cyclic voltammetry; lithium-ion battery.

Introduction

Lithium-ion batteries have found to be the most popular energy storage system over the last two decades [1-3], providing solutions to environmental issues and the growing demand for portable electronic devices as well as hybrid electric vehicles (HEVs) [4, 5].

Several lithium transition metal oxides have been functioned as the competitive intercalation cathode materials for their applications in rechargeable lithium-ion batteries (LIBs) [6-9]. Among them, layered rock-salt compound LiCoO_2 is established appropriate and efficient for commercial application in accordance with its higher theoretical capacity (274 mAhg^{-1}), high operating potential (~3.9 Volt), flat charge-discharge plateau, ease of synthesis, high electronic conductivity and excellent cycling ability [10-13]. However, certain limitations still persist with LiCoO_2 material, as extraction of more than fifty percent Li^+ ions from the material always destroy the crystal structure and thus capacity not more than 140 mAhg^{-1} are achievable under reversible condition. Besides this, the cobalt oxide material suffers from elevated cost and environmental incompatibility [9,14,15]. Therefore, for large-scale application, such as EVs and backup power system, alternating low cost cathode materials, having large faradic capacity and environmental compatibility, are highly desired.

Iron-based cathode materials are thus the ideal candidates for future LIBs taking into account of

manufacturing cost and environmental safety issues [16-18]. Among iron-based compounds, LiFePO_4 cathode material is regarded as the potential and promising candidate for future LIBs and thus intensively studied during last century [19-26]. However, limitation lies with this material due to its deprived electronic conductivity and sluggish Li^+ ion transport [27-31]. Electrical conductivity as well as transport properties of this material has been improved by proper doping with higher valent metal cations [32-37] or coating with conducting carbon additives in the cost of its intrinsic capacity [38-43]. Hence, searching for an alternate iron based cathode material having higher faradic capacity is urgently needed for high power lithium ion batteries.

In this paper, we report a promising and inexpensive cathode material of the formula, Li_2MZrO_4 (M = Fe, Mn) having theoretical capacity 238 mAhg^{-1} suitable for next generation high power rechargeable LIBs [44-49].

Experimental

Material synthesis procedure

Li_2MZrO_4 (M = Fe or Mn) materials were synthesized applying modified solid-state synthesis method [19, 50]. In order to synthesize 1.5 g of $\text{Li}_2\text{FeZrO}_4$, the stoichiometric amounts i.e.; 0.4927 g Li_2CO_3 (Sigma-Aldrich, USA, 99.9 %), 1.1995 g $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (Aldrich, USA, 99.9 %) and 0.8217 g ZrO_2 (Aldrich, USA, 99.9 %) were weighted. For

1.5 g of $\text{Li}_2\text{MnZrO}_4$, 1.025 g Li_2ZrO_3 (Aldrich, USA, 99.9 %) and 1.6491 g $\text{Mn(II)(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$ (Merck, USA, 99.5 %) were weighted. Before weighing and mixing, all the reagents were ground individually to make fine powder. After taking the stoichiometric amount of the reagents as mentioned above in a mortar pestle, small amount of pure acetone (Merck, USA, GR grade) was added to the mixture and ground them further to prepare a homogeneous mixture. The acetone was slowly evaporated out during grinding and the residual mixture was then taken in a highly crystallized alumina boat, placed inside a horizontal tubular furnace and calcined at 500 °C for 4 hours under nitrogen atmosphere. After cooling down to room temperature, the powder was ground again and sintered at 800 °C for 8 hours under nitrogen atmosphere for crystalline particle growth. Finally, the sintered materials ($\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$) were cool down to room temperature very slowly and preserved to reach out of moisture for further use.

Characterization

TGA (Thermal Gravimetric Analysis) of the precursor mixture was recorded with a Thermo Balance (Perkin Elmer, Sweden model number STA 6000) to establish the decomposition temperature. A curve, representing the percentage of weight loss versus temperature, was obtained after thermal treatment in the temperature region of 42 °C–933 °C at the rate of 20 °Cmin⁻¹ under continuous nitrogen gas flow.

The synthesized solid materials were characterized using powder X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Powder XRD pattern were recorded from a Ultima III Rigaku machine using Cu-K α ($\lambda=1.5406 \text{ \AA}$) as the radiation source in the range of $2\theta = 10^\circ\text{--}70^\circ$ with scan rate 5° min⁻¹. The particle size distribution and surface morphology was examined using a Scanning Electron Microscope (JEOL, Model-JSM-6360, UK).

In order to evaluate the electrochemical characteristics of the synthesized materials, the working electrode (cathode) was prepared as follows: first a slurry was made by mixing 80wt % of active material (Li_2MZrO_4 , M = Fe or Mn), 8wt % carbon black (Alfa Aesar, USA, 99.9 %), 8wt % graphite powder (Alfa Aesar, USA, 99.99 %) and 4wt % binder polyvinylidene fluoride (PVDF, Aldrich, USA, 99.9 %) in a solvent of N-methyl pyrrolidone (NMP) (Merck, USA, 99.5 %) [51–53]. The uniform slurry, as obtained, was then coated on an aluminum foil (1 cm²) and dried inside a vacuum oven at 60 °C. The coated foil was then pressed by a hydraulic press at 8–10 Tcm⁻² to attain better contact between the active material and the aluminum foil current collector [54–56]. Finally, the coated foil was dried overnight at 80 °C under vacuum to eliminate NMP completely in order to get the loading mass of the active materials, which was ~2.5 mg cm⁻². The dried electrode was used as cathode to fabricate a coin type cell, which is composed of lithium metal foil (Aldrich, USA, 99.9 %) as anode, 1M LiPF_6 (Alfa Aesar, 98 %) solution, prepared in ethylene carbonate (EC) (Aldrich, 99.9 %) and dimethyl carbonate (DMC) (Aldrich, 99.9 %) in 1:1 ratio as an electrolyte and a porous polypropylene (PP) film soaked with this electrolyte as the separator [57–59]. The coin type

cell was assembled inside a glove bag under argon atmosphere after complete replacement of air and moisture by pure argon gas. A computer controlled potentiostat/galvanostat, model VersaStatTMII (Princeton Applied Research) was used for electrochemical studies. The cyclic voltammograms (CVs) were recorded at a scan rate of 0.2 mVs⁻¹ with a cut-off limit 2 – 4.5 V vs. Li/Li⁺. The charge-discharge measurements were carried out with a current rate 0.1C.

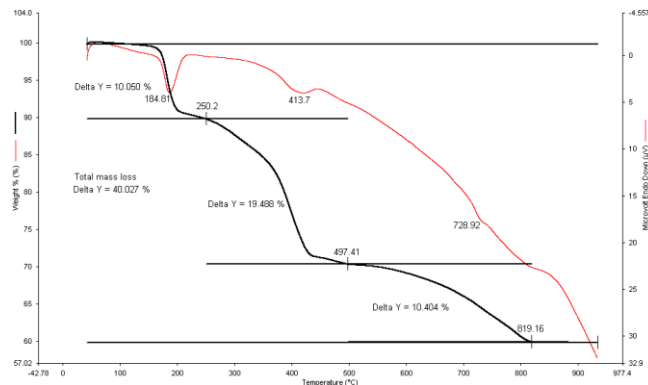


Fig. 1. TGA-DTA curve of the precursor mixture for synthesis of $\text{Li}_2\text{FeZrO}_4$.

Results and discussion

TGA-DTA analysis

Fig. 1 demonstrates the TGA-DTA curve of the precursor materials recorded under nitrogen environment. It is noticed from the illustration that the major weight loss has occurred mainly in three steps. In the first step within the temperature range between room temperature (RT) to 250 °C, 10 % weight loss was observed that is attributed owing to the elimination of humidity and water of crystallization from $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ crystals. In the second step, within the temperature range 250 °C–500 °C another 19.5 % weight loss has occurred, which is attributed due to the decomposition of $\text{Fe}(\text{C}_2\text{O}_4)$ and Li_2CO_3 . It is clear from the literature that pure Li_2CO_3 decomposes above 720 °C, but herein, it starts to disintegrate well below 720 °C within the above temperature range for being a eutectic mixture [60]. In the final step, within 800 °C the decomposition of carbonate and oxalate are accomplished and thereby a new material was produced. Based on the DTA-TGA study, the calcinations and sintering temperatures for the synthesis of zirconate materials are set at 500 °C for 4 hours and at 800 °C for 8 hours, respectively.

Powder XRD analysis

Powder XRD pattern of $\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$, illustrated in **Fig. 2** and **Fig. 3**, are recorded within the range, $2\theta = 10^\circ\text{--}70^\circ$ at scan rate of 5° min⁻¹ employing Cu-K α ($\lambda=1.5406 \text{ \AA}$) as the radiation source. The peak location and pattern were evaluated in comparison with the reported JCPDS data, file number 38-0281 for $\text{Li}_2\text{FeZrO}_4$ and 40-0360 for $\text{Li}_2\text{MnZrO}_4$, where an entire matching of peak positions was observed. However, a careful and systematic analysis of the XRD data using a software, called POWDIN, revealed that the present material ($\text{Li}_2\text{FeZrO}_4$)

belongs to tetragonal crystal structure with space lattice *P*-type and lattice parameters, $a = 4.1988 \text{ \AA}$ and $c = 9.0607 \text{ \AA}$ in contrast to the literature report of *I*-type lattice with lattice parameters, $a = 4.193 \text{ \AA}$ and $c = 9.003 \text{ \AA}$. Likewise, $\text{Li}_2\text{MnZrO}_4$ has tetragonal crystal structure with space lattice *P*-type and lattice parameters, $a = 4.2470 \text{ \AA}$ and $c = 9.2410 \text{ \AA}$, which exactly matches with the literature data.

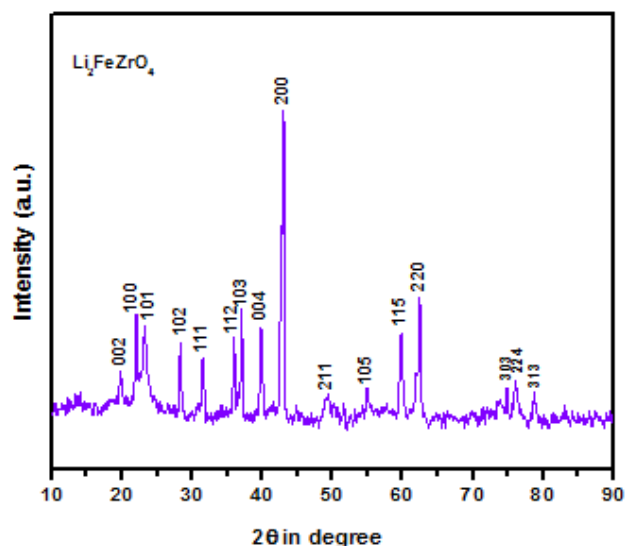


Fig. 2. Powder XRD pattern of $\text{Li}_2\text{FeZrO}_4$ sintered at $800 \text{ }^\circ\text{C}$.

Careful assessment of the XRD pattern reveals that the peaks for $\text{Li}_2\text{FeZrO}_4$ are very sharp, intense and the crystals are highly oriented along 200 planes, whereas peaks for $\text{Li}_2\text{MnZrO}_4$ are broaden and no specific orientation of the crystals are observed. The high-intense peaks are in favor of highly crystalline particle growth, whereas peak-broadening supports the formation of nano material.

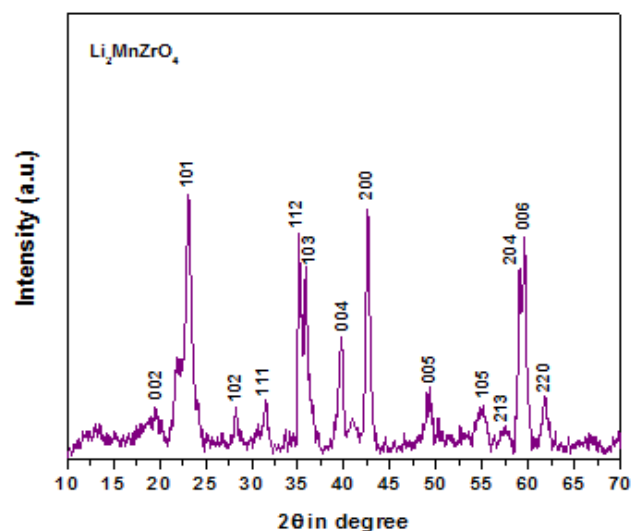


Fig. 3. Powder XRD pattern of $\text{Li}_2\text{MnZrO}_4$ sintered at $800 \text{ }^\circ\text{C}$.

SEM analysis

Scanning Electron Microscopy (SEM) was performed to investigate the particle size distribution and surface morphology of the synthesized materials. The SEM images,

presented in **Fig. 4**, clearly illustrate the arrangement of porous smaller size grains with large surface area, which ultimately influence the performance of the material. Moreover, SEM images clearly indicate that the particles are composed of nano and micron sizes, and their sizes lie between 200 nm to $1 \text{ }\mu\text{m}$. Further it is evident from the SEM images that $\text{Li}_2\text{MnZrO}_4$ particles are more evenly distributed and particle size distributions are more even and homogeneous, whereas, it is uneven and agglomerations among the particles are observed in case of $\text{Li}_2\text{FeZrO}_4$ material.

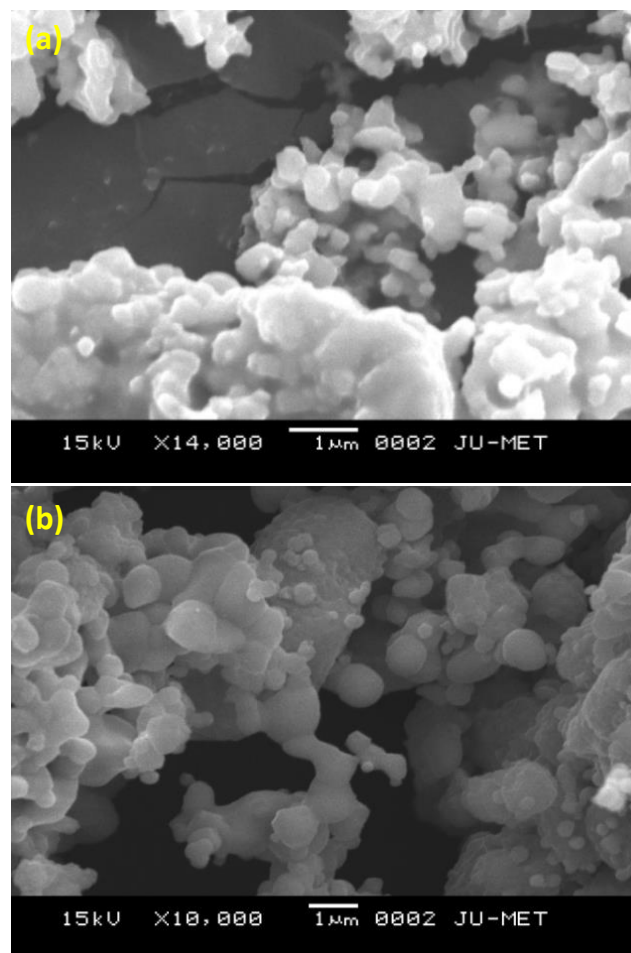


Fig. 4. SEM images of $\text{Li}_2\text{FeZrO}_4$ (a); and $\text{Li}_2\text{MnZrO}_4$ (b).

CV and charge-discharge study

For the potential application of Li_2MZrO_4 ($M = \text{Fe}$ or Mn) material, the cyclic voltammograms (CVs) were used to evaluate the electrochemical performance. The CVs were recorded with the aforementioned fabricated laboratory model cells within the potential window of $2.2\text{--}4.5$ volts vs. Li/Li^+ , at a scan rate of 0.2 mVs^{-1} and the corresponding $i\text{-v}$ graphs for $\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$ were in **Fig. 5**, respectively. The cyclic voltammograms clearly showed one pair of redox peaks within the specified window corresponding to the cathodic and anodic reactions. In principle, the reversibility of a redox system can be justified from the ratio of $i_{p,r}/i_{p,f}$, where, $i_{p,r}$ and $i_{p,f}$ are the backward and forward peak current, respectively; which is unity for a reversible process. Since the measurement of

cathodic peak current, in case of $\text{Li}_2\text{MnZrO}_4$, is difficult due to complexity in locating the proper baseline from which the peak current to be measured, the current ratios of the present systems are calculated using the empirical method of Nicholson [61] (Equation 1),

$$\frac{i_{p,r}}{i_{p,f}} = \frac{(i_{p,r})_0}{i_{p,f}} + 0.48 \frac{i_s}{i_{p,f}} + 0.086 \quad (1)$$

where, $(i_{p,f})$ is forward peak current, and $(i_{p,r})$ is reverse peak current and (i_s) is the measured current at the switching potential of the forward peak from the same baseline. The measured current values for both the systems are included in **Table 1**. From the ratio of backward and forward peak current, it is clear that both the systems are highly reversible.

Table 1. Ratio of the reverse and forward peak currents for reversibility test.

Cathode	$i_{p,f}$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	$(i_{p,r})_0$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	i_s ($\mu\text{A}\cdot\text{cm}^{-2}$)	$(i_{p,r})/(i_{p,f})$
$\text{Li}_2\text{FeZrO}_4$	114	109	49	1.24
$\text{Li}_2\text{MnZrO}_4$	131	63	116	1.00

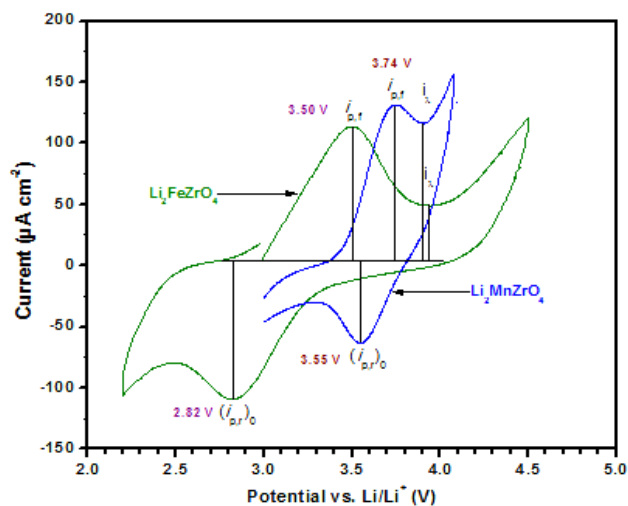


Fig. 5. Cyclic voltammograms of $\text{Li}_2\text{FeZrO}_4$ & $\text{Li}_2\text{MnZrO}_4$ vs. Li at the scan rate of 0.2 mVs^{-1} .

The peaks in the anodic scan are due to removal of first lithium ion from the compound, whereas, peaks in the reverse scan are due to insertion of first lithium ion in the matrix. Careful scrutiny of the CVs revealed that the redox peaks in case of iron substituted zirconium are very sharp compared to manganese substituted zirconium material. This clearly suggests that electronic conductivity of iron substituted zirconium is higher than that of manganese substituted zirconium material and thus the reaction kinetics is faster in case of $\text{Li}_2\text{FeZrO}_4$. On the other hand, the separation between anodic and cathodic peaks (ΔV) for both the materials are quite large, 0.70 V for $\text{Li}_2\text{FeZrO}_4$, whereas it is about 0.50 V for $\text{Li}_2\text{MnZrO}_4$, which indicates that the electrochemical behavior is controlled by diffusion steps. It is well known that the maximum rate of reaction (i_p) in a reversible diffusion controlled reaction will only be achieved if the sweeping potential cross beyond the formal potential and thus large peak potential difference is

expected. Again if the reaction is slow and the rate of electron transfer rather than the diffusion is the rate determining step, the sweep will continue further before the maximum reaction rate is observed. In the present study, large ΔV indicates that kinetics for both the materials are diffusion controlled and in case of $\text{Li}_2\text{FeZrO}_4$ having highest ΔV indicates that electron transfer rate rather than diffusion is the rate determining step. Therefore it may be concluded from the CVs that electron transfer reaction in $\text{Li}_2\text{MnZrO}_4$ is faster than $\text{Li}_2\text{FeZrO}_4$, which may reflect in the faradic capacity.

Coin cells using Li_2MZrO_4 ($M = \text{Fe}$ or Mn) cathode and lithium anode were galvanostatically charged and discharged between 2.2 to 4.5 volts vs. Li/Li^+ at room temperature. **Fig. 6** represents the charge and discharge profiles for 1st cycle at 0.1 C rates. The $\text{Li}_2\text{FeZrO}_4$ compound delivers a first cycle charge and discharge capacity of 93 and 89 mAhg^{-1} , respectively, whereas the $\text{Li}_2\text{MnZrO}_4$ compound delivers a first cycle charge and discharge capacity of 99 and 94 mAhg^{-1} , respectively. Both the compounds deliver a first cycle discharge capacity around 90 mAhg^{-1} , which is $\sim 76 \%$ of their theoretical capacity based on one lithium ion extraction. The discharge capacity can further be enhanced towards theoretical value by the formation of nano sized particles. It should be mentioned here that the discharge potential for both the compounds is similar, but the charging potential in case of $\text{Li}_2\text{MnZrO}_4$ compound is higher than $\text{Li}_2\text{FeZrO}_4$ and this might be due to higher interfacial resistance of the cell made out of $\text{Li}_2\text{MnZrO}_4$ compound.

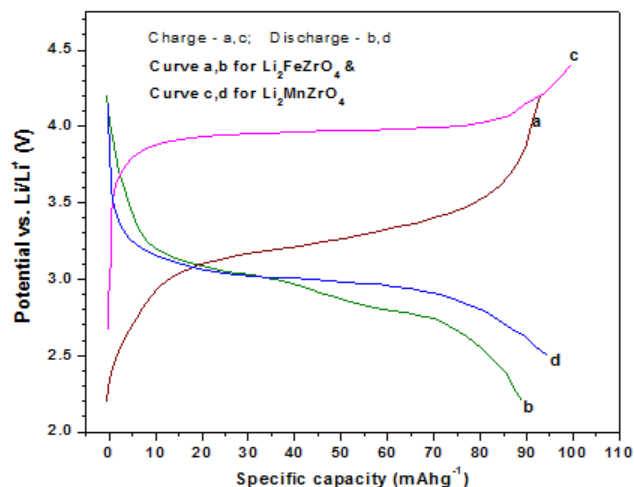


Fig. 6. Charge-discharge curve of $\text{Li}_2\text{FeZrO}_4$ & $\text{Li}_2\text{MnZrO}_4$ cathodes vs. Li anode at 0.1 C rates.

Conclusion

A new and novel cathode of the formula, Li_2MZrO_4 ($M = \text{Fe}$ or Mn), has been successfully synthesized by solid-state method based on cheaper and environment friendly precursors. Powder XRD pattern matches with the literature data and thus support the formation of pure crystalline material. SEM images revealed the formation of particles within nano to micron range. Cyclic voltammograms of the assembled cells using these materials as cathode display high reversibility and the electrochemical processes are controlled by diffusion step. The first cycle discharge

capacity delivered by these compounds is $\sim 90 \text{ mAhg}^{-1}$, which is 75 % of their theoretical capacity based on one lithium ion extraction and this can further be enhanced by synthesizing nano sized material. The discharge capacity of these materials can be further enhanced by extracting both the lithium ions in a large potential window by choosing a suitable electrolytic solution. Finally, cost effective, environment friendly lithium ion batteries are proposed out of these materials, as these compounds are non-toxic and inexpensive.

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